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16. ABSTRACT

In this paper it was demonstrated empirically that disinfection with ozone can be controlled by monitoring the exhuast gas ozone concentration exiting the contactor. This method is more reliable than measuring dissoloved ozone because of the inherent difficulties and inadequacies of the state-of-the-art dissolved residual techniques. The advantages of measuring exhaust gas ozone are summarized as follows:

- True ozone is being measured, free of interferences,
- Ozone demand of the effluent and transfer efficiency of the contactor are automatically accounted for in one measurement,
- The method is easily automated,
- Instruments are already available on the market for measuring ozone in the gas phase with accuracy, precision, and low level sensitivity and
- Ozone is more stable in the gaseous phase than in the liquid phase, and consequently the operator does not have to concern himself with dissipation of the ozone from the time it leaves the contactor to the time it arrives at the analyzer.

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Control of ozone disinfection by exhaust gas monitoring

Albert D. Venosa, Mark C. Meckes

The thrust of the U. S. Environmental Protection Agency's (EPA's) in-house research on ozone has been directed toward optimizing ozone contacting to achieve the desired bacteriological quality with the least amount of ozone applied. The reason is simply that ozone, which must be generated on-site, is energy intensive and, therefore, any effort at reducing the use of ozone will result in substantial savings in operating costs.

Exhaust gas monitoring has several advantages over measuring dissolved ozone, provided that the ratio of gas flow to liquid flow is constant.

Having established the bubble diffuser as the most efficient contactor of five generic types tested,[1-3] we deemed it necessary to determine how best to monitor and control applied dose as demand and flow fluctuated. We hypothesized that there was no reason why a compound loop control mechanism analogous to that used in the chlorination field could not be developed for ozone. Such a control mechanism would involve a flow signal, which would increase the rate of addition of ozone to the effluent, and a demand signal, which would increase the concentration of ozone applied. The problem confronting us was the lack of ability to measure true ozone residual in the process water. Conventional measurement techniques do not differentiate ozone from other oxidants, and without such differentiation a control mechanism would be impossible.

In a brief review of the literature, we found very little research has been done in this area. An EPA report published in August 1978[4] contained a global survey of all treatment plants (mostly drinking water) using ozone for disinfection and other uses. It reported that French plants incorporate a closed-loop control system by which the residual ozone level in the ozonated water is used to control the amount of ozone supplied to maintain that residual. In a symposium sponsored by the International Ozone Association in 1975,[5] several speakers discussed the need for measuring ozone in both the gas phase and the liquid phase. Nebel and Forde,[6] in discussing the principles of industrial and municipal odor control with ozone, demonstrated that by installing an ozone meter in the exhaust gas stack coming off the contactor, it was possible to detect small concentrations of ozone in the exhaust gas stream, and then feed signals to the generator to vary the ozone input to the contactor. Trussell[7] expressed a desire to be able to monitor ozone in the exhaust gas from the contactor to determine the efficiency of consumption and the amount of ozone needed to be destroyed before discharge to the ambient atmosphere. His primary interest, however, was measuring ozone in water for dose control purposes.

From the above it is clear that there are two variables that can be measured for the purpose of establishing an automatic, real-time monitoring tool: ozone residual in the liquid stream, and ozone concentration in the exhaust gas. Both of these variables represent unused ozone, the former being that amount of ozone transferred to the liquid but not reacted or decomposed, the latter being that amount of ozone not transferred to the liquid. The magnitude of both will depend on the demand of the liquid, the ozone transfer efficiency of the contactor, the concentration of ozone in the inlet gas, and the gas flow rate relative to the liquid flow rate. This paper will discuss measurement of ozone residual and exhaust gas relative to coliform destruction and attempt to demonstrate the superiority and reliability of exhaust gas measurements as a dose monitoring and control technique.

MATERIALS AND METHODS

Sources of secondary effluent. Secondary effluent was obtained from six different sources: the Fairfield Wastewater Treatment Plant, Fairfield, Ohio; the Indian Creek Wastewater Treatment Plant, Cincinnati, Ohio; the Loveland Wastewater Treatment Plant, Loveland, Ohio; the Mill Creek Wastewater Treatment Plant, Cincinnati, Ohio; the Muddy Creek Wastewater Treatment Plant, Cincinnati, Ohio; and the Sycamore Wastewater Treatment Plant, Cincinnati, Ohio. Fairfield, Mill Creek, and Muddy Creek are conventional activated sludge treatment plants. Loveland and Sycamore are contact sta-

bilization plants, and Indian Creek uses rotating biological contactors to treat municipal wastewater. Of the six treatment plants, five receive raw wastewater of municipal origin. The sixth, Mill Creek, receives wastewater with a high concentration of industrial wastes (about 50% of the organic loading by weight).

Approximately 20 m^3 of a given effluent was collected in a tank truck on the day of an experiment, or the day before, and transported to the EPA Test and Evaluation Facility adjacent to the Mill Creek treatment plant. When an effluent was collected the day before an experiment, it was recirculated in the tank truck for a minimum of 1 hour before initiation of the experiment.

Ozone generation. Ozone was generated from oxygen in a plate type corona discharge generator. Oxygen flow to the ozonator was maintained at a constant 33 L/min. Liquid flow was a constant 75 L/min, resulting in a gas-to-liquid flow ratio of 0.44. Changes in the applied dose were accomplished by varying the concentration of ozone in the gas flow, that is, by increasing or decreasing the power applied to the generator.

Ozone contactor. The ozone contactor used was a bubble diffuser with three columns connected in series. Its design and operating characteristics are fully described elsewhere.[2]

Sampling. All effluent samples were grab samples and were analyzed for total and soluble chemical oxygen demand (TCOD and SCOD), total organic carbon (TOC), total suspended solids (TSS), and turbidity by techniques described in "Standard Methods."[8] Total Kjeldahl nitrogen (TKN), ammonium nitrogen (NH_4^+-N), and nitrite-nitrogen (NO_2^--N) were measured according to "Methods for Chemical Analysis of Wastes"[9] and nitrate-nitrogen (NO_3^--N) according to Kamphake *et al.*[10] Ozone concentration in the inlet and exhaust gases was periodically determined iodometrically[8,11] and continuously by ultraviolet adsorption analyzers. Ozone residual (as total residual oxidant) was measured by the reverse titration standard iodometric method for chlorine residual[8] using the amperometric end point.

Samples collected for bacteriological analysis were assayed for total and fecal coliforms by the standard membrane filtration (MF) method,[8] using 0.45 μm GN-6 membrane filters. All chemical and bacteriological samples were collected from a sample tap located at the bottom of the contactor's third column.

Procedure. The six treatment plant effluents were segregated into three distinct groups according to their demand characteristics. Five applied dose levels were computed for each of the three groupings and related in such a way that the same coliform numbers would result in each group after each dose level. In other words, the five dose levels (labeled A through E) were relative in the sense that each one theoretically yielded equivalent coliform densities consistent with effluent quality so long as dose was varied by changing the ozone concentration in the inlet gas stream and maintaining a constant gas-to-liquid flow ratio. The five relative dose levels for each of the treatment plant groupings are listed in Table 1. Five replicate samplings of each effluent were tested according to a randomized collection schedule. An entire replicate run, consisting of one effluent receiving the five dose levels, required approximately 4 hours to complete. The order in which the five dose levels were applied was randomized to minimize any trend in wastewater effluent quality in a given day.

Table 1—Relative dose scheme for the three treatment plant groupings used in the study.

Relative dose	Theoretical log total coliform density	Actual dose, mg/L		
		Group I[a]	Group II[b]	Group III[c]
A	5.0	1.3	2.3	5.1
B	4.0	3.3	5.1	10.0
C	3.0	5.0	7.6	15.0
D	2.0	6.7	9.8	20.5
E	1.0	8.6	12.4	25.1

[a] Effluent Sources: Indian Creek Plant, Loveland Plant, and Muddy Creek Plant.
[b] Effluent Sources: Fairfield Plant and Sycamore Plant.
[c] Effluent Source: Mill Creek Plant.

RESULTS

Effluent quality. Table 2 summarizes the physical-chemical and bacteriological characteristics of the effluent sources prior to ozonation. The Mill Creek effluent contained substantially higher amounts of TCOD and TOC than any of the other effluents. This was caused by the high proportion of industrial components present in the raw wastewater entering the plant.

Effect of absorbed ozone on coliform numbers. We have shown previously[2,3] that total and fecal coliform levels in a given effluent can be predicted if the demand properties of the effluent and the absorbed ozone dose are known. Figure 1 is a graph of the log total and fecal coliform numbers in the six effluents as a function of the amount of ozone transferred to the effluents. The data were averaged over the five replicate runs. Clearly, dose responses in five of the six effluents were similar. The coliform decline in the sixth effluent, at the Mill Creek Treatment Plant, deviated significantly from the others, reflecting the substantially higher demand characteristics of that effluent and indicating that such responses are not universally predictable or applicable. Thus, attempts to monitor disinfection efficiency by measuring ozone transfer may lead to erroneous results.

Effect of ozone residual on coliform numbers. Figure 2 is a plot of total and fecal coliform numbers in the six effluents as a function of ozone residual in the liquid.

Table 2—Secondary effluent characterization of the six treatment plants prior to ozonation.

Parameter	Effluent Source					
	Fairfield mean (range)	Indian Creek mean (range)	Loveland mean (range)	Muddy Creek mean (range)	Mill Creek mean (range)	Sycamore mean (range)
TCOD, mg/L	39 (63–22)	26 (48–16)	39 (57–30)	29 (45–16)	74 (103–53)	38 (56–26)
TOC, mg/L	5.6 (11.1–1.3)	5.2 (9.0–2.2)	6.8 (13.8–3.7)	5.0 (9.0–1.2)	19.6 (29.9–13.9)	8.3 (12.7–4.6)
TSS, mg/L	4.1 (13.2–1.4)	9.2 (36.8–1.8)	8.3 (34.0–3.7)	3.8 (9.2–0.4)	11.5 (25.0–2.8)	8.6 (18.8–3.0)
TKN, mg/L	5.3 (12.3–1.9)	1.7 (7.2–0.5)	13.8 (17.8–9.8)	1.5 (4.5–0.6)	18.7 (31.0–8.1)	7.5 (17.6–4.4)
NH_4^+-N, mg/L	4.3 (12.4–0.1)	0.3 (0.7–<0.1)	11.7 (18.6–6.4)	0.8 (3.6–<0.1)	19.3 (31.8–7.3)	5.6 (7.3–4.5)
NO_2^--N, mg/L	0.6 (1.8–<0.1)	0.2 (1.1–<0.1)	0.5 (1.3–0.1)	0.2 (0.9–<0.1)	0.6 (2.6–<0.1)	0.5 (1.1–<0.1)
NO_3^--N, mg/L	7.5 (13.8–4.3)	7.5 (14.1–3.2)	0.1 (0.2–<0.1)	6.0 (8.8–3.0)	0.2 (0.7–<0.1)	2.5 (5.8–<0.1)
Turbidity, JTU	2.5 (5.3–1.0)	1.7 (7.2–0.5)	13.8 (17.8–9.8)	1.5 (4.5–0.6)	18.7 (31.0–8.1)	7.5 (17.6–4.4)
pH	(8.3–7.3)	(8.4–7.9)	(8.2–7.4)	(8.1–7.3)	(7.9–7.4)	(7.9–7.2)
$\log_{10}$TC/100 mL	5.41 (6.51–4.28)	5.59 (6.11–5.08)	6.56 (7.27–6.16)	5.41 (6.33–4.65)	5.72 (6.84–4.68)	6.43 (6.86–6.08)
$\log_{10}$FC/100 mL	4.69 (5.60–3.30)	4.43 (5.00–3.76)	5.80 (6.36–5.15)	4.59 (5.21–3.79)	4.75 (6.18–3.85)	5.67 (5.94–5.46)

Again, the data were averaged over the five replicate runs. Response patterns are similar to those shown in Figure 1, although the deviations in the Mill Creek effluent were not as great. Use of ozone residual in the liquid as a real-time monitoring tool may be appropriate if it is expected that fluctuations in wastewater quality are relatively minor. However, as will be shown below, even if the quality has not changed significantly, the presence of compounds or substances that interfere with

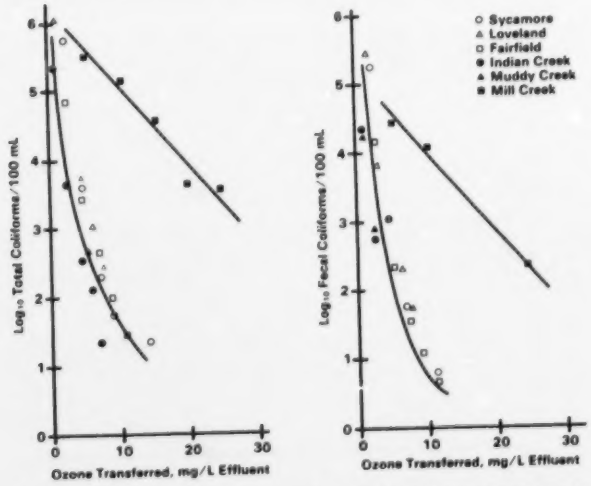

Figure 1—Effect of ozone transferred on coliform densities in secondary effluents: (a) total coliforms, (b) fecal coliforms. Each point is an average of 5 data points.

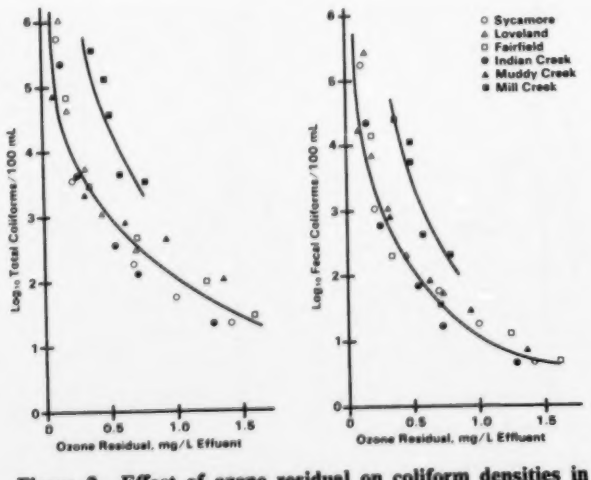

Figure 2—Effect of ozone residual on coliform densities in secondary effluents: (a) total coliforms, (b) fecal coliforms. Each point is an average of 5 data points.

the measuring technique may argue against use of ozone residual as the primary control technology.

Effect of exhaust gas ozone on coliform numbers. Results of plotting log coliform numbers as a function of ozone concentration in the exhaust gas are presented in Figure 3. Clearly, the data from all six treatment plants fit the indicated curve quite well, suggesting strongly that measurement of ozone in the exhaust gas from the contactor may be an excellent control strategy. There is a very important restriction, however, that must be incorporated when using this strategy: the gas-to-liquid flow ratio must be held constant at all times. The reason is that the mass transfer efficiency of the contactor decreases markedly as the gas flow increases.[2] Thus, an increase in gas flow relative to liquid flow may result in a higher exhaust gas ozone concentration without any corresponding increase in mass transfer or coliform reduction. In contrast, by maintaining a constant gas-to-liquid ratio and varying the power (or frequency) to the generator, the increase in ozone transferred will be almost in direct proportion to the higher ozone concentration in the inlet gas, up to the limit defined by Henry's Law. A higher exhaust gas level will occur also, but only after more ozone has been transferred to the water. Thus, an increase in coliform reduction will necessarily take place.

Interferences in residual measurement. To demonstrate further the inferiority of monitoring ozone residual in the liquid to control disinfection, all 125 data points from 5 of the 6 treatment plant effluents (the Mill Creek effluent was excluded) were used to plot log total coliforms in the effluent as a function of ozone residual. Results are shown in Figure 4. Although a clear trend is noted, four data points (represented by open squares) stand out as significant outlyers. On studying carefully the computer printout of the raw data, we discovered

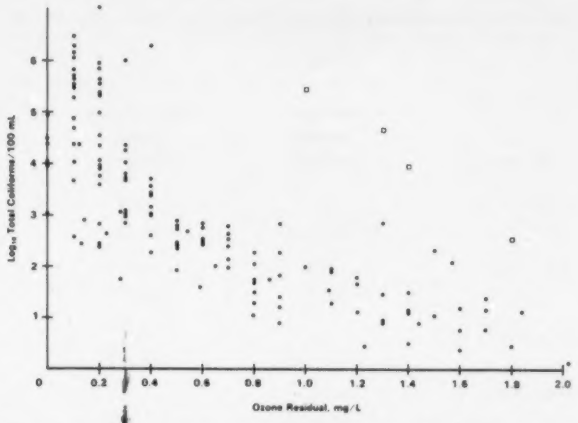

Figure 4—Effect of ozone residual on total coliforms in five of the six effluents (all data).

that these high coliform and ozone residual values all occurred in the same run with the same effluent (the Muddy Creek effluent). The only unusual feature of this effluent on that date was a high concentration of manganese, approximately 0.8 mg/L. This amount exceeded the normal levels measured on all other days by more than 25-fold. According to "Standard Methods,"[8] oxidized forms of manganese give positive interferences in all methods for total available chlorine (the method we were using for ozone), including amperometric titration. Thus, if an operator is measuring ozone residual by standard, state-of-the-art techniques, he could be misled on days when positive interferences are present unexpectedly in the effluent. On such days coliform discharge limitations could be exceeded.

We made a similar plot of log total coliform numbers versus exhaust gas ozone (Figure 5). The Mill Creek effluent is included in this plot. Clearly, no outlyers are

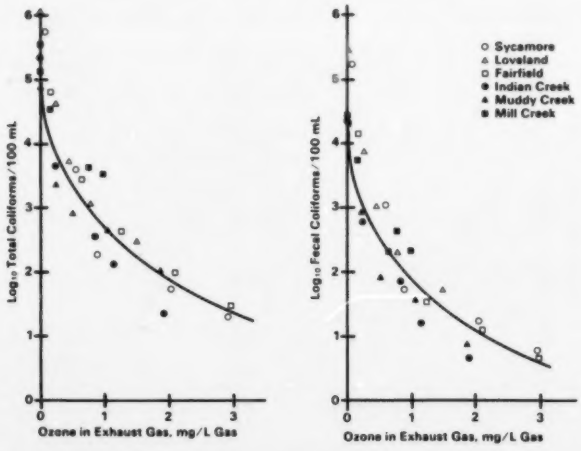

Figure 3—Effect of ozone concentration in exhaust gas on coliform densities in secondary effluents: (a) total coliforms, (b) fecal coliforms. Each point is an average of five data points.

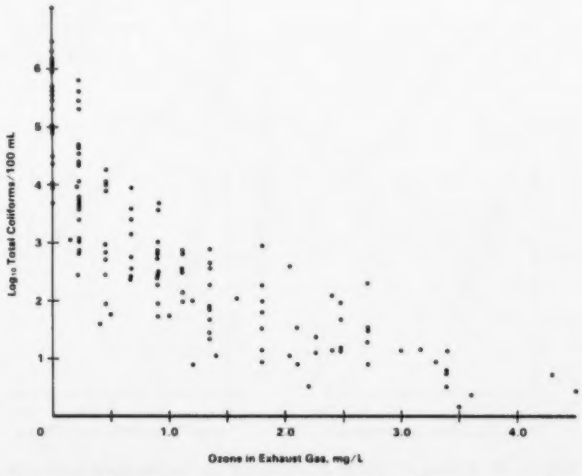

Figure 5—Effect of ozone concentration in exhaust gas on total coliforms in all six effluents (all data points).

observable on the graph because true ozone is being measured in the gas phase. This again confirms the usefulness and reliability of exhaust gas monitoring for control of ozone disinfection at a secondary treatment plant.

SUMMARY AND CONCLUSIONS

In this paper we have demonstrated empirically that disinfection with ozone can be controlled by monitoring the exhaust gas ozone concentration exiting the contactor. This method is more reliable than measuring dissolved ozone because of the inherent difficulties and inadequacies of state-of-the-art dissolved residual techniques. The advantages of measuring exhaust gas ozone are summarized as follows:

- True ozone is being measured, free of interferences,
- Ozone demand of the effluent and transfer efficiency of the contactor are automatically accounted for in one measurement,
- The method is easily automated,
- Instruments are already available on the market for measuring ozone in the gas phase with accuracy, precision, and low level sensitivity, and
- Ozone is more stable in the gaseous phase than in the liquid phase, and consequently the operator does not have to concern himself with dissipation of the ozone from the time it leaves the contactor to the time it arrives at the analyzer.

It must be emphasized that exhaust gas monitoring is only applicable if the gas-to-liquid flow ratio is held constant. The control loop is then envisioned as follows: a flow-proportional measurement signals a change in the gas flow from the ozone generator to the contactor as liquid flow changes, thereby keeping the ratio constant; and, as ozone concentration in the exhaust gas changes either as a result of a change in demand of the effluent or a change in flow conditions, a signal is sent to the ozone generator to change the power or frequency input accordingly. Thus, disinfection is controlled easily, reliably, and with confidence. The effect this control strategy has on the cost of ozone production has yet to be evaluated. The data presented in this paper were obtained using a plug flow bubble diffuser contactor. There is no reason to believe, however, that the control strategy would not be applicable to other types of ozone contactors as well.

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